The opinion in support of the decision being entered today is *not* binding precedent of the Board.

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE BOARD OF PATENT APPEALS
AND INTERFERENCES

Ex parte JOHN SKOUFIS

Appeal 2007-2364
Application 09/879,613[1]
Technology Center 3700

Decided: July 20, 2007

Before TEDDY S. GRON, CAROL A. SPIEGEL, and MARK NAGUMO, *Administrative Patent Judges*.

NAGUMO, *Administrative Patent Judge*.

DECISION ON APPEAL

A. Introduction

Skoufis appeals under 35 U.S.C. § 134 from the final rejection of claims 1, 3–5, 9, and 12, all of the pending claims. We have jurisdiction

---

[1] The real party in interest is identified as Illinois Tool Works, Inc. (Br. at 2.)

under 35 U.S.C. § 6(b). We REVERSE and enter a NEW GROUND OF REJECTION under 37 C.F.R. § 41.50(b).

The claimed subject matter relates to a packaged sterilized sponge said to be useful for scrubbing semiconductor wafers in clean rooms.

The Examiner has relied on the following art as evidence of unpatentability under 35 U.S.C. § 103:

Paley	5,988,371	23 Nov. 1999
Onodera	6,012,576	11 Jan. 2000

B. Findings of Fact

The following findings of fact and those set out in the Discussion are supported by a preponderance of the evidence of record. To the extent a finding of fact involves a conclusion of law, it may be treated as such.

1. The application on appeal, 09/879,613, was filed on 12 June 2001, claiming the benefit under 35 U.S.C. § 119(e) of provisional application 60/210,969, which was filed 12 June 2000.

2. According to the Specification, Skoufis discovered that by soaking sponges made from polyvinylalcohol ("PVA") in a dilute solution of hydrogen peroxide in deionized water, bacterial growth is inhibited. (Specification at 4, 2d full paragraph.)

3. According to the Specification, the invention provides the unexpected benefit that the hydrogen peroxide-deionized water solution "tends to deteriorate fairly rapidly" leaving only water and oxygen as decomposition products, "without any metal ions or debris of any kind" that would compromise the cleanliness of the ultraclean sponges. (Specification at 4, last paragraph.)

4. Skoufis asserts that the prior art, which uses hydrogen peroxide at concentrations of, for example, 1% to 5%, can result in unwanted impurities, such as methyl [sic: metal?] ions. (Specification at 5, last paragraph.)

5. Skoufis teaches that such problems can be avoided by using "a substantially lower concentration of about 0.05 to 1%, preferably about 0.1% . . . thereby avoiding the deleterious effects of the higher concentrations." (Specification at 5, last paragraph.)

6. The Specification does not appear to disclose any other values for the upper end of the hydrogen peroxide concentration.

7. In Skoufis's words, "The amount of hydrogen peroxide is selected so as to be low enough to give reasonable assurance that it will actually decompose into its components by the time the package is opened to remove the material for use." (Specification at 5, 2d paragraph.)

8. According to Skoufis, the low end of the hydrogen peroxide concentration is sufficient to kill bacteria, while "[t]he high value is one at which metal ions or other impurities developed are at intolerable [sic: maximum tolerable] levels." (Specification at 7, 2d paragraph.)

9. Skoufis emphasizes that "highly pure de-ionized water and ultra-pure semiconductor grade hydrogen peroxide" are used in his invention. (Specification at 7, 1st paragraph.)

10. According to Skoufis, the soaked sponges can be stored in sealed plastic bags for six months or one year and more "without significant increase in contamination." (Specification at 8, 3d and 5th full paragraphs.)

11. The Specification does not describe any working examples of the invention or of the prior art.

12. Claim 9 on appeal reads:

> A packaged PVA sponge for use in clean rooms,
>
> said cleaning article having particulate, metal ion and anionic counts at or below the values specified for a clean room,
>
> said package comprising a sealed flexible plastic bag,
>
> said sponge being positioned in said bag, and containing a quantity of de-ionized water,
>
>> said de-ionized water containing hydrogen peroxide in a concentration effective to kill and retard the growth of bacteria in said sponge, said amount being low enough to substantially ensure decomposition of said hydrogen peroxide in a relatively short period of time after the container is sealed and being between 0.05 and 0.5% by volume.

13. Independent claims 1 and 5 are similar, being drawn to methods of packaging the PVA sponge; but they do not recited the particle, metal ion and anionic count limitations, and the end points of the range of hydrogen peroxide concentration are recited to be "around" or "about" 0.05 and 0.5% by volume.

14. Dependent claims 4 and 12 recite that the "volume" and the concentration by volume, respectively, of hydrogen peroxide is around 0.1%.

Onodera[2]

15. Onodera describes methods of storing brushes used during the manufacturing process of electronic devices to wash, make smooth, etc., semiconductor wafers and similar substrates. (Onodera at 1:6–15.)

16. The brushes are said to be fibrous or sponge-like, and to be made from synthetic polymers such as polyvinyl alcohol. (Onodera at 1:39–44.)

17. Fine particles, such as those that can be produced when a brush is dried and then rewetted, are said to be a contamination problem for semiconductor wafer surfaces. (Onodera at 1:51 to 2:2.)

18. Microorganisms growing in wet brushes exposed to the atmosphere are also disclosed to be a contamination problem for semiconductor wafer surfaces. (Onodera at 2:3–11.)

19. Onodera discloses that these problems may be solved by storing the brush in a tightly sealed container after soaking the brush in water and filling the container with an antibacterial liquid. (Onodera at 2:66 to 3:5.)

20. According to Onodera, the brush can be stored for "a very long time, such as a few months or about half a year." (Onodera at 3:7; 4:54–57.)

21. Examples of bactericidal liquids are said to include an aqueous solution of 1 to 5% hydrogen peroxide. (Onodera at 3:8-9.)

22. Onodera describes containers that are rigid enough to support the sponge-like member so it does not experience any "deforming stress." (Onodera at 4:57–58.)

---

[2] U.S. Patent 6,012,576, issued 11 January 2000, to Naoko Onodera, based on application 08/684,859, filed 25 July 1996.

23. Onodera does not appear to expressly describe the use of deionized water or maximum allowable metal ion or anion concentrations.

Paley[3]

24. Paley describes a cleaning kit of extremely clean wipers and a container of cleaning fluid that may be comprised of deionized water and a bactericide (Paley at 10:5–20) packaged in a flexible sealed plastic bag (*id.* at 2:34–56).

25. Paley claims the benefit of priority under 35 U.S.C. § 120 to 12 September 1995, via intervening divisional and continuation applications, and also the benefit of an ultimate continuation-in-part parent application filed on 10 March 1995.

Hydrogen Peroxide

26. The properties of solutions of hydrogen peroxide are summarized in *The Dispensatory of the United States of America*, 25th ed., Arthur Osol et al., eds., 670 (1960) ("Dispensatory"): a copy of the article is attached to this Decision and has been entered in the record of this application.

27. According to the Dispensatory, "**Incompatibilities.**—Hydrogen peroxide is decomposed by reducing agents including most organic matter. It reacts with oxidizing agents to liberate oxygen. Metals, metallic salts, light, agitation and heat increase its decomposition." (Dispensatory at 671, col. 1.)

[3] William R. Paley et al., U.S. Patent 5,988,371, issued 23 November 1999.

28. According to the Dispensatory:

> [t]he germicidal activity of hydrogen peroxide is generally greatly overestimated; it persists only as long as oxygen is being released. Although in relatively dilute solution it will eventually destroy many of the pathogenic microorganisms, its action is extremely slow * * * [i]f allowed sufficient time, relatively small quantities are highly efficient. Heinemann (*J.A.M.A.*, 1913, 60, 1603) reached the conclusion from his experiments that 3 teaspoonfuls of the official solution, after 6 hours' exposure will destroy 99 per cent of the bacteria present in a liter of drinking water; this quantity makes about a 1:1000 solution of hydrogen peroxide.

(Dispensatory at 671, paragraph bridging the columns.)

<u>Integrated Circuit Fabrication</u>

29. According to a technical encyclopedia article, "[t]he integrated-circuit fabrication process is quite sensitive to both particulate and impurity contamination. . . . To minimize impurity contamination effects, the chemicals, solvents, and metals which are used must be of the highest possible purity (electronic grade)." Bob L. Gregory and Eugene A. Irene, *Integrated Circuits, Fabrication, in* 9 *McGraw-Hill Encyclopedia of Science & Technology* 260, 260 (7th ed. 1992). (A copy of this article is attached to this Decision and has been entered in the record of this application.)

<u>The Examiner's Rejection</u>

30. The Examiner found that Onodera discloses every limitation of the claimed invention "except for the container to be a flexible plastic bag and the specific degree of range of the hydrogen peroxide." (Examiner's Answer ("Answer") at 3.)

31. In particular, the Examiner found that Onodera taught the use of its packaged sponges in a clean room, the use of deionized water, and "particulate, metal ion and ionic counts at or below the values specified for clean room." (Answer at 3.)

32. The Examiner found that Paley teaches a flexible plastic bag as a container allowing easier shipping and handling. (Answer at 3.)

33. The Examiner concluded that the choice of "material [PVA] of the cleaning article" would have been obvious because it would have been the selection of a known material on the basis of its suitability for the intended use. (Answer at the paragraph bridging 3–4.)

34. The Examiner concluded further that the recited range of hydrogen peroxide composition would have been obvious as a routine optimization of the general conditions of the claims. (Answer at 4.)

Skoufis's Arguments

35. Skoufis states that claims 1 and 3 stand or fall together; that claims 4 and 5 do not stand or fall together or with any other claims; and that claims 9 and 12 stand or fall together. (Br. at 6.)[4]

36. However, Skoufis does not appear to argue the separate patentability of any of the claims or groups of claims.

37. Skoufis's principal argument is that "[n]either of the cited references discloses the concept of using very low concentrations of hydrogen peroxide

[4] References are to Appellant's Substitute Appeal Brief ("Br."), filed 19 April 2006.

to ensure rapid decomposition of the hydrogen peroxide and thus prevent it from being a source of impurities." (Br. at 8.)

38. According to Skoufis, Onodera "strongly implies" that the bactericide should remain effective for a very long time, and hence teaches that concentrations of 1% to 5% are required to obtain that result. (Br. at 9-10.)

39. Skoufis argues further that Paley supports its interpretation of Onodera by teaching that, in order to maintain the effectiveness of the bactericide, it should be isolated from the wipers until just prior to their use. (Br. at 11–12.)

40. Skoufis argues further that Onodera does not teach the use of deionized water, nor particulate, metal ion, or anionic counts. (Br. at 12-13.)

41. Skoufis concludes that the claimed invention is counterintuitive and unobvious (Br. at 12) and that it has "created a new result," namely the rapid decomposition of hydrogen peroxide, which results in a sponge free of hydrogen peroxide contaminant and "without the metallic ions which can be caused by prolonged contact between the hydrogen peroxide and the sponge." (Br. at 13.)

C. Discussion

Obviousness is a legal conclusion based on findings of fact. *In re Gartside*, 203 F.3d 1305, 1316, 53 USPQ2d 1769, 1778 (Fed. Cir. 2000). During prosecution, the PTO gives claims "their broadest reasonable construction in light of the specification as it would be interpreted by one of ordinary skill in the art." *Phillips v. AWH Corp.*, 415 F.3d 1303, 1316, 75 USPQ2d 1321, 1329 (Fed. Cir. 2005) (en banc) (internal quotation and

citation omitted). However, limitations are not to be read from the specification into the claims. *Renishaw PLC v. Marposs Societa' per Azioni*, 158 F.3d 1243, 1248–49, 48 USPQ2d 1117, 1120–21 (Fed. Cir. 1998). Once a prima facie case of obviousness has been established, the burden shifts to the applicant to come forward with evidence of unexpected results. *In re Piasecki*,745 F.2d 1468, 1472, 223 USPQ 785, 788 (Fed. Cir. 1984).

We begin with two preliminary observations. First, although Skoufis states that certain claims stand or fall separately from others, we find no colorable argument that the claims are drawn to patentably distinct subject matter other than the statements that certain limitations are not disclosed by the references (FF 35 and 36). Accordingly, we shall analyze patentability with regard to claim 9, which is reproduced *supra*, and we hold that argument as to the separate patentability of subject matter as claimed separately has been waived in this appeal. Second, we note that references Onodera and Paley are prior art under 102(e), but that Skoufis has not attempted to antedate these references. We hold such arguments also to have been waived in this appeal.

As to the merits, the Examiner has not directed our attention to any specific disclosures in Onodera of the use of deionized water, or low metal ion or anionic "counts" at or below acceptable clean room values. Nor have we found such disclosures. However, as shown by the article from the *McGraw-Hill Encyclopedia of Science and Technology* cited *supra* (FF 29), semiconductor wafer processing for integrated circuit manufacture is notoriously sensitive to contamination by particulates and chemical impurities. We do not find it credible—and we note that Skoufis has not denied—that anyone skilled in the relevant arts would have used water that

was not free from particles, metal ions, or anions, for the processing of wafers in a clean room. In this regard, we also note the notorious sensitivity of hydrogen peroxide to metal salts, illustrated by the passage from the Dispensatory cited *supra* (FF 27). This provides further evidence, if any be needed, that the use of deionized water as a diluent for hydrogen peroxide in the context of a wipe or sponge intended for use in a clean room would have been considered so ordinary that a disclosure directed to skilled workers might well not mention it. *Cf. Hybritech Inc. v. Monoclonal Antibodies, Inc.*, 802 F.2d 1367, 1384, 231 USPQ 81, 94 (Fed. Cir. 1986) ("a patent need not teach, and preferably omits, what is well known in the art") We understand that it can be difficult to find evidence of ordinary practices, because they are seldom described in technical literature: but it is error to mischaracterize a reference. At the same time raising formal issues that lack substantive merit neither advances prosecution nor enhances the credibility of opposing arguments.

On the matter of the concentration of hydrogen peroxide recited in the claims on appeal, we find that the Examiner has skipped over the Office's burden to establish an evidentiary foundation for the *prima facie* case of obviousness. In particular, the Examiner has not supported the finding that hydrogen peroxide concentration over the range recited in the claims is a known result-effective variable that would have been obvious to optimize. Establishing such a foundation is particularly important when the applicant's specification, as here, expressly distinguishes its range (0.05 to 1% hydrogen peroxide by volume in the original claims and in the Specification at 5) from the prior art, which Applicant describes as 1% to 5% hydrogen peroxide. Moreover, Applicant asserts that the use of its hydrogen peroxide

concentrations avoids "deleterious effects" associated with the higher range used in the prior art (FF 3–5; Specification at 5). The burden is on the Examiner to establish an adequate basis to question the adequacy of Appellant's disclosure. *In re Marzocchi*, 439 F.2d 220, 223–4, 169 USPQ 367, 370 (CCPA 1971). Assertions in a disclosure must be met with evidence, not by mere counter-assertion or examiner argument.

The efficacy of dilute hydrogen peroxide as a germicide is well known, as shown by the disclosure in the Dispensatory that a 1:1000 solution is effective (FF 28). Thus, we have no difficulty finding that when Onodera recites that "Examples of bactericidal liquid include an aqueous solution of 1 to 5% hydrogen peroxide" (FF 21; Onodera at 3:8-9; emphasis added), one of ordinary skill in the art would have recognized that still more dilute samples would have been expected to be bactericidal, and therefore efficacious. Moreover, the Examiner found that Onodera is concerned with substantially the same problem as Skoufis—namely, the necessity of sterilizing and storing sponges for clean room use for a period of several months to half a year or so (FF 20). We emphasize that this period is comparable to the period addressed by Skoufis (six month to a year or more: FF 10). Thus, there is a sound basis for the finding that the artisan would have reasonably expected success using lower concentrations of hydrogen peroxide as a germicide that are within the range recited by Applicant.

We reject Skoufis's contention that Onodera and Paley teach away from the claimed invention. We find nothing in either reference that warns a person of ordinary skill in the art not to use low concentrations of hydrogen peroxide known to be germicidal. Cf. *Para-Ordnance Manufacturing, Inc. v. SGS Importers International, Inc.*, 73 F.3d 1085, 1090, 37 USPQ2d 1237,

1241 (Fed. Cir. 1995) (to teach away, a reference must state that it "should not" or "cannot" be used in combinations with the other reference.). Moreover, we are not persuaded that the Examiner erred by relying on Paley for the suggestion to use a flexible plastic bag as a container for the sponges. Skoufis's arguments that Paley keeps the bactericidal solution separate from the wipers does not detract from the teaching that sealable plastic bags are suitable for contamination-free storage of the wipers.

Thus, a sound basis exists to conclude that a prima facie case of obviousness exists.

Skoufis alleges unexpected results in his disclosure. (FF 3–5; Specification at 4.) However, Skoufis does not provide any experimental results. Evidence of expected results must be weighed against evidence of unexpected results. *In re Young*, 927 F.2d 588, 591, 18 USPQ2d 1089, 1091 (Fed. Cir. 1991). The mere allegation of unexpected results, unsupported by experimental evidence, carries less weight than the evidence of the Dispensatory. We find Skoufis's specification insufficient to rebut the prima facie case of obviousness.

Although we are reluctant to burden the Examiner with the potential for continued prosecution in this case pursuant to 37 C.F.R. § 41.50(b), the Examiner's failure to establish the necessary evidentiary foundation for the legal conclusion of obviousness leaves us with little choice. Had the information not been so readily available, we should not have hesitated simply to reverse.

In the event of further prosecution, we suggest that the Examiner and Skoufis consider whether an adequate written description exists in the

original Specification for the recitation of "0.5%" (claim 9) and "around 0.5%" (claims 1 and 5) hydrogen peroxide. The cases of *Lockwood v. American Airlines*, 107 F.3d 1565, 1571-72, 41 USPQ2d 1961, 1966 (Fed. Cir. 1997) ("Entitlement to a filing date does not extend to subject matter which is not disclosed but would be obvious over what is expressly disclosed. It extends only to that which is disclosed . . . The question is not whether a claimed invention is an obvious variant of that which is disclosed in the specification. Rather, a prior application itself must describe an invention, and do so in sufficient detail that one skilled in the art can clearly conclude that the inventor invented the claimed invention as of the filing date sought.") and *In re Wertheim*, 541 F.2d 257, 261–67, 191 USPQ 90, 95 -100 (CCPA 1976) (discussing the written description requirement) provide appropriate guidance for evaluating the facts of this case. We express no opinion on the resolution of these questions, but note that the outcome may affect the analysis of whether "about 0.5%" hydrogen peroxide reads on the 1% hydrogen peroxide disclosed Onodera, or whether it remains the result of mere optimization of a result effective variable.

D. Conclusion

In view of the record and the foregoing considerations, it is:

ORDERED that the Examiner's rejection of claims 1, 3–5, 9, and 12 as unpatentable under 35 U.S.C. § 103 over the combined teachings of Onodera and Paley is REVERSED;

FURTHER ORDERED that a new ground of rejection is entered pursuant to 37 C.F.R. § 41.50(b).

37 CFR § 41.50(b) also provides that the appellant, WITHIN TWO MONTHS FROM THE DATE OF THE DECISION, must exercise one of the following two options with respect to the new ground of rejection to avoid termination of the appeal as to the rejected claims:

(1) *Reopen prosecution.* Submit an appropriate amendment of the claims so rejected or new evidence relating to the claims so rejected, or both, and have the matter reconsidered by the examiner, in which event the proceeding will be remanded to the examiner. . . .

(2) *Request rehearing.* Request that the proceeding be reheard under § 41.52 by the Board upon the same record.

REVERSED AND NEW GROUND OF REJECTION UNDER 37 CFR § 41.50(b)

mg:

KRAMER LEVIN NAFTALIS & FRANKEL LLP
INTELLECTUAL PROPERTY DEPARTMENT
1177 AVENUE OF THE AMERICAS
NEW YORK NY 10036

THE DISPENSATORY OF THE UNITED STATES OF AMERICA

25th Edition

ARTHUR OSOL, PH.G., B.S., M.S., PH.D.

PROFESSOR OF CHEMISTRY AND DIRECTOR OF THE DEPARTMENT AND SCHOOL OF CHEMISTRY, PHILADELPHIA COLLEGE OF PHARMACY AND SCIENCE; MEMBER OF THE COMMITTEE OF REVISION OF THE UNITED STATES PHARMACOPEIA

GEORGE E. FARRAR, JR., B.S., M.D., F.A.C.P.

MEDICAL DIRECTOR, WYETH LABORATORIES, INC.; ASSOCIATE PROFESSOR OF MEDICINE, TEMPLE UNIVERSITY SCHOOL OF MEDICINE AND HOSPITAL; MEMBER OF THE COMMITTEE OF REVISION OF THE UNITED STATES PHARMACOPEIA

WITH

KARL H. BEYER, JR., B.S., PH.D., M.D.

LECTURER IN PHARMACOLOGY, GRADUATE SCHOOL OF MEDICINE, UNIVERSITY OF PENNSYLVANIA, AND TEMPLE UNIVERSITY SCHOOL OF MEDICINE; ASSISTANT DIRECTOR OF RESEARCH, SHARP & DOHME DIVISION, MERCK & CO., INC.

DAVID K. DETWEILER, V.M.D., M.S.

ASSOCIATE PROFESSOR OF VETERINARY PHARMACOLOGY, SCHOOL OF VETERINARY MEDICINE, GRADUATE SCHOOL OF ARTS AND SCIENCES, AND THE GRADUATE SCHOOL OF MEDICINE, UNIVERSITY OF PENNSYLVANIA

JOHN H. BROWN, V.M.D.

PRODUCTION MANAGER, MARIETTA BIOLOGICAL LABORATORY, WYETH LABORATORIES, INC.

ROBERTSON PRATT, A.B., PH.D.

PROFESSOR OF PHARMACOGNOSY AND ANTIBIOTICS, UNIVERSITY OF CALIFORNIA COLLEGE OF PHARMACY

HEBER W. YOUNGKEN, PH.M., PH.D., SC.D.

RESEARCH PROFESSOR OF PHARMACOGNOSY AND BOTANY, MASSACHUSETTS COLLEGE OF PHARMACY; MEMBER OF THE COMMITTEE OF REVISION OF THE UNITED STATES PHARMACOPEIA.

Editor Emeritus

HORATIO C. WOOD, JR., M.D., PH.M.

PROFESSOR EMERITUS OF PHARMACOLOGY, PHILADELPHIA COLLEGE OF PHARMACY AND SCIENCE; EMERITUS PROFESSOR, GRADUATE SCHOOL OF MEDICINE, UNIVERSITY OF PENNSYLVANIA

Based on the Fifteenth Revision of The United States Pharmacopeia, the Tenth Edition of The National Formulary, The British Pharmacopœia, 1953, the First Edition of the International Pharmacopoeia, Volumes I and II

DROIT ET AVANT

Philadelphia *Montreal*

J. B. LIPPINCOTT COMPANY

THE DISPENSATORY OF THE UNITED STATES OF AMERICA

25th Edition

Third Printing

Distributed in Great Britain *by*
PITMAN MEDICAL PUBLISHING CO., Limited
London

Library of Congress
Catalog Card Number
7-31327

Printed in the United States of America

HYDROGEN PEROXIDE SOLUTION. U.S.P. (B.P.)

Hydrogen Dioxide Solution, Liquor Hydrogenii Peroxidi

"Hydrogen Peroxide Solution contains, in each 100 ml., not less than 2.5 Gm. and not more than 3.5 Gm. of H_2O_2. Suitable preservatives, totaling not more than 0.05 per cent, may be added." *U.S.P.* The B.P. solution is required to contain not less than 5.0 per cent w/v and not more than 7.0 per cent w/v of H_2O_2, corresponding to about 20 times its volume of available oxygen.

B.P. Solution of Hydrogen Peroxide. Hydrogen Peroxide; "Peroxide." Hydrogenium Peroxydatum Solutum; Solutum Hydrogenii Peroxydati Officinale; Solutio Bioxydi Hydrogenii. *Fr.* Soluté officinal d'eau oxygénée; Eau oxygénée officinale. *Ger.* Wasserstoffsuperoxydlösung. *It.* Acqua ossigenata; Biossido d'idrogeno. *Sp.* Solución de bióxido de hidrógeno; Agua oxidenada; *Solución de Peróxido de Hidrógeno.*

Hydrogen peroxide was first prepared by Thénard, in 1818, by treating barium peroxide with hydrochloric acid. The same reaction, but using either sulfuric or phosphoric acid so as to precipitate the barium ion, was for many years employed in the commercial production of hydrogen peroxide solution. A somewhat similar reaction between sodium peroxide and sulfuric acid has also been utilized commercially, the by-product sodium sulfate being precipitated with the aid of sodium fluoride.

The most important method, however, for preparing hydrogen peroxide in large quantities and high concentrations involves electrolysis of solutions of sulfuric acid containing one or more of its salts. Thus, by electrolysis of a concentrated solution containing potassium bisulfate, ammonium sulfate and sulfuric acid, oxidation of sulfate to persulfate occurs at the anode and solid potassium persulfate is separated. Treatment of this salt with strong sulfuric acid and steam hydrolyzes the persulfate with formation of hydrogen peroxide which may be distilled off, in concentrations as high as 35 per cent H_2O_2. If desired, further concentration may be effected through two stages of distillation, the final product containing up to 90 per cent of H_2O_2.

Such high test peroxide was developed during World War II, principally by the Germans, as a source of energy for the operation of submarine engines and for propulsion of rockets, torpedoes and other military missiles. It is claimed that in the presence of suitable catalysts it dissociates instantly into 5000 times its volume of steam and oxygen. Under standard conditions of temperature and pressure one volume of 90 per cent hydrogen peroxide releases 413 volumes of oxygen; the official hydrogen peroxide solution releases approximately 10 times its volume of oxygen. The high-test peroxide can be shipped in aluminum drums and tank cars; if the liquid is not permitted to become contaminated no decomposition occurs. If allowed to come in contact with combustible matter a fire may result. It is miscible with many organic liquids with which the official solution is immiscible. For data on corrosion and stability studies of concentrated hydrogen peroxide see Bellinger *et al.* (*Ind. Eng. Chem.*, 1946, **38**, 310).

Absolute H_2O_2 has been obtained by extraction with ether and evaporation of the latter under reduced pressure and at low temperature. The melting point of the pure compound is about —2° and the boiling point is 152.1°.

Because of the instability of hydrogen peroxide various stabilizing agents are commonly added. Small concentrations of such substances as acetanilid, oxyquinoline, tetrasodium pyrophosphate and acids serve to stabilize all concentrations of hydrogen peroxide solutions. Various metals and metallic salts, on the other hand, catalyze the decomposition of the substance; alkalinization also accelerates decomposition.

The official hydrogen peroxide solution may be prepared by diluting any of the stronger solutions, sufficient preservative being incorporated to stabilize the diluted solution. Even the 3 per cent solution is a powerful oxidizing agent, reacting with many oxidizable substances. On the other hand, in the presence of a stronger oxidant, hydrogen peroxide solution serves as a reducing agent; thus, potassium permanganate is reduced by it, oxygen being evolved from the peroxide.

Hydrogen peroxide forms with urea a solid compound called *"urea peroxide"* or *"carbamide peroxide"* capable of yielding over 35 per cent of H_2O_2. In some countries the compound finds use as a preservative for milk; 0.1 per cent of it is said to keep milk for 72 hours. Under the name *Thenardol* (named for Thénard, discoverer of hydrogen peroxide) a solution of this substance in anhydrous glycerin, stabilized with 8-hydroxyquinoline, has been found useful in treating infections of the eye, ear, mouth and skin (Brown *et al., New Eng. J. Med.*, 1946, **234**, 468; *Ann. Allergy*, 1946, **4**, 33; *J.-Lancet*, 1947, **67**, 405; *Arch. Otolaryng.*, 1948, **48**, 327; and others). The action of the compound depends on the evolution of hydrogen peroxide when in contact with water. It is supplied as *Glycerite of Hydrogen Peroxide with Carbamide* (International Pharmaceutical Corp.). Urea peroxide is used in industry as an oxidizing, bleaching and polymerizing agent in non-aqueous solutions.

Description.—"Hydrogen Peroxide Solution is a colorless liquid, odorless, or having an odor resembling that of ozone. It is acid to litmus and to the taste and produces a froth in the mouth. It usually deteriorates upon standing or upon protracted agitation, and rapidly decomposes when in contact with many oxidizing as well as reducing substances. When rapidly heated, it may decompose suddenly. It is affected by light. Its specific gravity is about 1.01." *U.S.P.*

Standards and Tests.—*Identification.*—On adding a drop of potassium dichromate T.S. to a mixture of 1 ml. of hydrogen peroxide solution, 10 ml. of water containing 1 drop of diluted sulfuric acid, and 2 ml. of ether, an evanescent blue color is produced in the aqueous layer; on agitation and standing the color passes into the ether layer. *Non-volatile residue.*—Not over 30 mg. from 20 ml. of hydrogen peroxide solution, the latter being evaporated on a water bath and the residue dried 1 hour at 105°. *Acidity.*—25 ml. of solution requires not more than 2.5 ml. of 0.1 *N* sodium

hydroxide for neutralization, using phenolphthalein T.S. as indicator. *Arsenic.*—The limit is 2 parts per million. *Barium.*—No turbidity results on adding 2 drops of diluted sulfuric acid to 10 ml. of hydrogen peroxide solution. *Heavy metals.*—The limit is 5 parts per million. *Limit of preservative.*—Not more than 50 mg. from 100 ml. of hydrogen peroxide solution on extracting the latter with a mixture of chloroform and ether. *U.S.P.*

Assay.—A 2-ml. portion of hydrogen peroxide solution is mixed with water and diluted sulfuric acid and titrated with 0.1 *N* potassium permanganate. The following reaction takes place: $5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow 5O_2 + 2MnSO_4 + K_2SO_4 + 8H_2O$. Each ml. of 0.1 *N* potassium permanganate represents 1.701 mg. of H_2O_2. *U.S.P.*

Incompatibilities.—Hydrogen peroxide is decomposed by reducing agents including most organic matter. It reacts with oxidizing agents to liberate oxygen. Metals, metallic salts, light, agitation and heat increase its decomposition.

Uses.—Hydrogen peroxide is used as an antiseptic, wound cleanser and deodorant. In solution it is slowly decomposed, liberating a portion of its oxygen. All tissues, including pus and blood, contain an enzyme, catalase, which releases oxygen. Evidently this nascent oxygen has a powerful oxidizing effect and thereby destroys many forms of organic matter. In the presence of these catalyzing agents, the antibacterial powers of the drug are greatly reduced. Effervescence is much more rapid on wounds, denuded areas and mucous membranes than on unbroken skin. Upon the system generally hydrogen peroxide does not, and cannot, exert any physiological action, because it cannot exist in the blood. Studies of intravenous administration in hypoxic animals failed to demonstrate any value and often the condition was aggravated by gas embolism or methemoglobin formation (Lorincz *et al.*, *Anesthesiology,* 1948, **9**, 162).

Antiseptic.—The most important use for this agent is as an antibacterial agent. The germicidal activity of hydrogen peroxide is generally greatly overestimated; it persists only as long as oxygen is being released. Although in relatively dilute solution it will eventually destroy many of the pathogenic microorganisms, its action is extremely slow, unless the solution be fairly concentrated. Gifford found that a neutral solution containing 15 per cent by volume of H_2O_2 (therefore stronger than the official solution) would destroy anthrax spores after 5 minutes' exposure, and pyogenic cocci in 1 minute, but that the same solution when diluted with 4 parts of water did not kill the pyogenic cocci after 30 minutes. Traugott found that 1 per cent by weight of H_2O_2 killed typhoid bacilli in 5 minutes and staphylococci in 15 to 30 minutes. On the other hand, if allowed sufficient time, relatively small quantities are highly efficient. Heinemann (*J.A.M.A.*, 1913, **60**, 1603) reached the conclusion from his experiments that 3 teaspoonfuls of the official solution, after 6 hours' exposure will destroy 99 per cent of the bacteria present in a liter of drinking water; this quantity makes about a 1:1000 solution of hydrogen peroxide. In the presence of organic matter the compound is so rapidly broken down that it is much less efficient (see review by Haase, *Pharmazie,* 1950, **5**, 436).

The addition of hydrogen peroxide solution has been recommended as an emergency method for the preservation of milk. It effects a partial or complete sterilization of the milk and quickly disappears, being dissociated into water and oxygen. The use in milk and cream has been common in Great Britain. As it was first suggested by Budd, products so preserved are sometimes called "buddized."

Cleanser.—Hydrogen peroxide solution is used in medicine as a means of cleansing wounds, suppurating ulcers, and the like. Its value in these conditions is probably more due to removing organic detritus, which forms a breeding place for the microorganisms, than to its antibacterial action. Its styptic effect—probably due to the activation of the fibrin ferment of the blood and consequent more rapid coagulation—as well as its relatively harmless nature make it a very popular antiseptic for household use. In inflammatory conditions of the external auditory canal, a dilution with 3 parts of water is a valuable cleanser prior to the instillation of the appropriate therapeutic agent according to the etiology of the condition. Without thorough cleansing of the canal, no chemotherapeutic agent can be effective. In cases with fecal impaction, after rectal instillation of warm liquid petrolatum at bed time, an enema of hydrogen peroxide solution diluted with 3 parts of water is often useful. In root canals of teeth or other dental pulp cavities, hydrogen peroxide diluted with an equal volume of water is used; zinc peroxide (*q.v.*) is also employed. It has sometimes been injected into deep cavities for the purpose of cleansing by irrigation and determining the presence of pus, which will be signalized by effervescence; the method, however, must be used with caution, because if there is not a free vent for the gas sufficient pressure may be generated within the cavity to cause serious local results and even air embolism. Because of its lack of toxicity it is a favorite disinfectant for application to various mucous membranes (see also use of "urea peroxide" above), especially those of the nose and throat. In diphtheria or tonsilitis the official solution may be applied undiluted, by means of either an atomizer or cotton applicator. Diluted with equal parts of water it is often employed as a gargle in pharyngitis, or as a mouth wash in stomatitis, but prolonged use causes irritation of the buccal mucous membrane. Diluted with 1 or more parts of water it has been used as a vaginal douche. Internally the solution has been used with success by Goodman (*Pennsylvania M. J.*, 1910) and others, in the treatment of hyperchlorhydria (gastritis). It has been claimed that it diminishes the acidity of the gastric juice, increases the secretion of mucus and exercises an antiseptic action in the stomach.

Campbell and Cherkin (*Science,* 1945, **102**, 535) found that heating pyrogenic solutions of

gelatin at 100° for 1 to 2 hours in the presence of 0.1 molar concentration of hydrogen peroxide resulted in destruction of the pyrogens; this finding has been applied practically in preparing certain non-pyrogenic solutions.

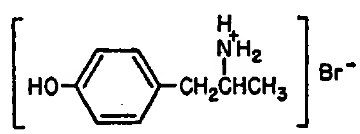
For bleaching hair, the undiluted official solution is used, but with care. Prolonged contact with skin causes erythema, which is transient, but a concentrated solution, as one of 30 per cent, causes a burn with a white eschar. ▽

For external use, hydrogen peroxide solution is applied topically as required to skin and mucous membranes. It should be noted that the B.P. solution is approximately twice the strength of the U.S.P. preparation and should be diluted with at least an equal volume of water for most uses. When taken internally, the usual *dose* is 4 ml. (approximately 1 fluidrachm) of the U.S.P. solution.

Storage.—Preserve "in tight, light-resistant containers, preferably at a temperature not above 35°." *U.S.P.*

HYDROXYAMPHETAMINE HYDROBROMIDE. U.S.P.

p-(2-Aminopropyl)phenol Hydrobromide, Hydroxyamphetaminium Bromide



Paredrine Hydrobromide (*Smith, Kline & French Labs.*).

The base of this sympathomimetic agent differs from amphetamine only in having a hydroxyl group in the para position of the benzene ring. Hydroxyamphetamine may be synthesized from the oxime of *p*-methoxyphenyl acetone, or by interaction of *p*-nitrobenzyl chloride and a salt of nitroethane, or by interaction of anisaldehyde and nitroethane (Hoover and Hass, *J. Org. Chem.*, 1947, **12**, 501). The hydrobromide is obtained by neutralization of the base with hydrobromic acid.

Description.—"Hydroxyamphetamine Hydrobromide occurs as a white, crystalline powder. Its solutions are slightly acid to litmus, having a pH of about 5. One Gm. of Hydroxyamphetamine Hydrobromide dissolves in about 1 ml. of water and in about 2.5 ml. of alcohol. It is slightly soluble in chloroform and almost insoluble in ether. Hydroxyamphetamine Hydrobromide melts between 189° and 192°." *U.S.P.*

Standards and Tests.—*Identification.*—(1) A purple color is produced on adding 0.5 ml. of ferric chloride T.S. to a solution of 10 mg. of hydroxyamphetamine hydrobromide in 10 ml. of water. (2) An intense blue color forms on adding 2 mg. of hydroxyamphetamine hydrobromide to a solution of 500 mg. of ammonium molybdate in 10 ml. of sulfuric acid (similar amino compounds such as amphetamine and methamphetamine, which lack a phenolic hydroxyl, do not give this reaction). (3) Hydroxyamphetamine base separated from the salt melts between 127° and 129°. (4) A pale yellow precipitate, slightly soluble in ammonia T.S., is produced on adding silver nitrate T.S. to a solution of 10 mg. of hydroxyamphetamine hydrobromide in 10 ml. of water, acidified with 1 ml. of diluted nitric acid. *Loss on drying.*—Not over 0.5 per cent, when dried at 105° for 2 hours. *Residue on ignition.*—Not over 0.1 per cent. *Nitrogen content.*—Not less than 5.9 per cent and not more than 6.2 per cent of N, when determined by the Kjeldahl method. *Bromide content.*—Not less than 33.6 per cent and not more than 35.2 per cent of Br, when determined by the Volhard method. *U.S.P.*

Uses.—The introduction of the *p*-hydroxyl group on the aromatic nucleus of amphetamine markedly alters its pharmacodynamic properties (for general discussion see monograph on *Sympathomimetic Amines*, in Part II). Thus, hydroxyamphetamine is 2- to 4-fold more active as a pressor agent, is relatively inactive when administered orally, does not have as long a duration of action and is devoid of central nervous system stimulation. By comparison, amphetamine is a less potent pressor agent, is active when administered orally, has a prolonged duration of action and is a useful euphoriant (Beyer, *Physiol. Rev.*, 1946, **26**, 169). Axelrod (*J. Pharmacol.*, 1954, **110**, 315) reported that whereas *d*-amphetamine is slowly excreted and metabolized at a rate of about 8 per cent per hour, the overall clearance of hydroxyamphetamine from the blood was at a rate of 40 per cent per hour. About 30 per cent of the intravenously administered drug was excreted as such and an additional 30 per cent was eliminated in a conjugated form.

Hydroxyamphetamine has been employed as the hydrobromide for use as a nasal decongestant and as a mydriatic agent. According to Powell and Hyde (*J. Kansas Med. Soc.*, 1938, **39**, 525) the agent is mydriatic, not cycloplegic; thus, there is no loss of accommodation or alteration of intraocular tension (see also Gettes, *Arch. Ophth.*, 1950, **43**, 446). Griffith (*U. S. Nav. M. Bull.*, 1945, **44**, 284) found hydroxyamphetamine to be useful in the prevention or treatment of bradycardia induced by a hyperirritable carotid sinus. Patients with heart block and Adams-Stokes syndrome were relieved of syncopal attacks by administration of 10 mg. every 3 hours orally (Green and Bennett, *Am. Heart J.*, 1945, **30**, 415). In 45 patients with established attacks of paroxysmal auricular tachycardia, the attacks were terminated in 30 minutes to 20 hours by administering 10 mg. of hydroxyamphetamine every 1 to 3 hours or 20 mg. every hour for 3 doses. Ordinarily one is not concerned about serious toxicity of such agents except as arise from cardiovascular symptomatology or excessive effects such as headache, palpitation, substernal discomfort, sweating, nausea and vomiting.

Administration.—For external use, 1 or 2 drops of the 1 per cent solution made isotonic with boric acid is applied to the conjunctival sac as a mydriatic. In the nose the 1 per cent solution made isotonic with sodium chloride is used as a vasoconstrictor in the form of a spray, drops or on a tampon; 2 to 5 drops are applied 4 or 5 times daily. For irrigation of the paranasal sinuses, a 0.25 per cent solution in sterile isotonic solution

McGRAW-HILL ENCYCLOPEDIA OF Science & Technology

9

ICE-LEO

c 1992

7th Edition

An international reference work in twenty volumes including an index

McGraw-Hill, Inc.
New York St. Louis San Francisco Auckland Bogotá Caracas Lisbon London Madrid Mexico
Milan Montreal New Delhi Paris San Juan São Paulo Singapore Sydney Tokyo Toronto

1234567890 DOW/DOW 998765432

Library of Congress Cataloging in Publication data

McGraw-Hill encyclopedia of science & technology : an international reference
work in twenty volumes including index. — 7th ed.
p. cm.

Includes bibliographical references and index.
ISBN 0-07-909206-3
1. Science—Encyclopedias. 2. Technology—Encyclopedias.
I. Title: McGraw-Hill encyclopedia of science and technology.
II. Title: Encyclopedia of science & technology.
III. Title: Encyclopedia of science and technology.
Q121.M3 1992 503—dc20 91–36349
CIP

ISBN 0-07-909206-3 {SET}

the bilateral Laplace transform of the kernel. It has been shown that the result is correct if, for example, $E(s)$ is the infinite product in Eq. (10), where $c \geqq 0$

$$E(s) = e^{bs-cs^2} \prod_{k=1}^{\infty} \left(1 - \frac{s}{a_k}\right) e^{s/a_k} \qquad (10)$$

and the series of real constants

$$\sum_{k=1}^{\infty} a_k$$

converges.

For example, if $K(x) = e^{-x}$, then Eq. (4) is the Laplace transform. Expressed as a convolution transform as in Eq. (3), it becomes Eq. (11), where G is

$$e^x F(e^x) = \int_{-\infty}^{\infty} G(x-y)\Phi(e^{-y})\, dy \qquad (11)$$

given in the above list as entry K. The bilateral Laplace transform of this kernel is the familiar gamma function, Eq. (12), whose reciprocal has a well-

$$\Gamma(1-s) = \int_{-\infty}^{\infty} e^{-st}G(t)\, dt = \int_0^{\infty} e^{-t}t^{-s}\, dt \qquad (12)$$

known expansion in the form of Eq. (10). In Eq. (13)

$$E(s) = \frac{1}{\Gamma(1-s)} = e^{-\gamma s} \prod_{k=1}^{\infty} \left(1 - \frac{s}{k}\right) e^{s/k} \qquad (13)$$

γ is Euler's constant. In the present example Eq. (9) becomes Eq. (14), or if $e^{-x} = t$, Eq. (15) may be

$$e^{-\gamma D} \prod_{k=1}^{\infty} \left(1 - \frac{D}{k}\right) e^{D/k} e^x F(e^x) = \Phi(e^{-x}) \qquad (14)$$

$$\lim_{k\to\infty} \frac{(-1)^k}{k!} F^{(k)}\left(\frac{k}{t}\right)\left(\frac{k}{t}\right)^{k+1} = \Phi(t) \qquad (15)$$

written. This familiar inversion formula also serves to illustrate the operator O_t appearing in Eq. (2). In the present case the operator is a differential one, and the parameter t is an integer k which tends to ∞. SEE CONFORMAL MAPPING; INTEGRATION.

David V. Widder

Bibliography. M. I. Akhiezer, *Lectures on Integral Transforms*, 1988; L. C. Andrews and B. K. Shivamoggi, *Integral Transforms for Engineers and Applied Mathematicians*, 1987; O. I. Marchev, *Handbook of Integral Transforms of Higher Transcendental Functions*, 1983; K. B. Wolf, *Integral Transforms in Science and Engineering*, 1979.

Integrated circuits

Miniature electronic circuits produced within and upon a single semiconductor crystal, usually silicon. Integrated circuits range in complexity from simple logic circuits and amplifiers, about ½₀ in. (1.3 mm) square, to large-scale integrated circuits up to about ½ in. (12 mm) square. They can contain millions of transistors and other components that provide computer memory circuits and complex logic subsystems such as microcomputer central processor units. SEE SEMICONDUCTOR; SILICON.

Since the mid-1960s, integrated circuits have become the primary components of most electronic systems. Their low cost, high reliability, and speed have been essential in furthering the wide use of digital computers. Microcomputers have spread the use of computer technology to instruments, business machines, automobiles, and other equipment. Other common uses of large-scale integrated circuits are in pocket calculators and electronic watches. For analog signal processing, integrated subsystems such as FM stereo demodulators and switched-capacitor filters are made. SEE CALCULATORS; DIGITAL COMPUTER; ELECTRONICS; MICROCOMPUTER.

Integrated circuits consist of the combination of active electronic devices such as transistors and diodes with passive components such as resistors and capacitors, within and upon a single semiconductor crystal. The construction of these elements within the semiconductor is achieved through the introduction of electrically active impurities into well-defined regions of the semiconductor. The fabrication of integrated circuits thus involves such processes as vapor-phase deposition of semiconductors and insulators, oxidation, solid-state diffusion, ion implantation, vacuum deposition, and sputtering.

Generally, integrated circuits are not straightforward replacements of electronic circuits assembled from discrete components. They represent an extension of the technology by which silicon planar transistors are made. Because of this, transistors or modifications of transistor structures are the primary devices of integrated circuits. Methods of fabricating good-quality resistors and capacitors have been devised, but the third major type of passive component, inductors, must be simulated with complex circuitry or added to the integrated circuit as discrete components. SEE TRANSISTOR.

Simple logic circuits were the easiest to adapt to these design changes. The first of these, such as inverters and gates, were produced in the early 1960s primarily for miniaturization of missile guidance computers and other aerospace systems. Analog circuits, called linear integrated circuits, did not become commercially practical until several years later because of their heavy dependence on passive components such as resistors and capacitors. The first good-quality operational amplifiers for analog computers and instruments were produced in 1966. SEE AMPLIFIER; ANALOG COMPUTER; LOGIC CIRCUITS.

TYPES OF CIRCUITS

Integrated circuits can be classified into two groups on the basis of the type of transistors which they employ: bipolar integrated circuits, in which the principal element is the bipolar junction transistor; and metal oxide semiconductor (MOS) integrated circuits, in which the principal element is the MOS transistor. Both depend upon the construction of a desired pattern of electrically active impurities within the semiconductor body, and upon the formation of an interconnection pattern of metal films on the surface of the semiconductor.

Bipolar circuits are generally used where highest logic speed is desired, and MOS for largest-scale integration or lowest power dissipation. Linear circuits are mostly bipolar, but MOS devices are used extensively in switched-capacitor filters. High-performance bipolar transistors and complementary MOS (CMOS) transistors have been combined on the same chip

Although these LSI circuits are being used in calculators, automobiles, instruments, appliance controls and many other applications, realization of their potential is just beginning. As the power of the computer is captured in the relatively inexpensive integrated circuit, the role of integrated circuits will continue to expand rapidly.

Ron Burghard; Youssef El-Mansy; Neil Berglund

Fabrication

Integrated-circuit fabrication begins with a thin, polished slice of high-purity, single-crystal semiconductor (usually silicon) and employs a combination of physical and chemical processes to create the integrated-circuit structures described above. Junctions are formed in the silicon slice by the processes of thermal diffusion or high-energy ion implantation. Electrical isolation between devices on the integrated circuit is achieved with insulating layers grown by thermal oxidation or deposited by chemical deposition. Conductor layers to provide the necessary electrical connections on the integrated circuit are obtained by a variety of deposition techniques. Precision lithographic processes are used throughout the fabrication sequence to define the geometric features required.

Requirements. The integrated-circuit fabrication process is quite sensitive to both particulate and impurity contamination. Airborne particulates must be minimized during the fabrication sequence, since even small (1-micrometer) particles on the wafer surface can cause defects. A particulate-free fabrication ambient is normally achieved by the use of vertical laminar-flow clean rooms or benches (**Fig. 12**). Lint-free garments are worn to minimize operator-borne particulates. To minimize impurity contamination effects, the chemicals, solvents, and metals which are used must be of the highest possible purity (electronic grade). Yellow light is necessary in the clean room because of the ultraviolet-sensitive photolithographic processes employed.

The precision and cleanliness requirements of integrated-circuit processing necessitate high discipline throughout the process sequence. This is achieved by extensive operator training, in-process tests and inspection with continual feedback, and a high degree of equipment calibration and control. The physical environment and operator attitude in an integrated-circuit fabrication facility are important factors for successful operation.

Processes. The basic relationship between the major processes in integrated-circuit fabrication is shown schematically in **Fig. 13**. Film formation is normally followed by impurity doping or lithography. Lithography is generally followed by etching, which in turn is followed by impurity doping or film formation. Impurity doping is normally followed by film formation or lithography. A complete integrated-circuit process sequence requires many cycles through the flow diagram in Fig. 13. For example, metal gate CMOS requires seven cycles through lithography. The complete flow time for a CMOS process is approximately 2 to 6 weeks, depending on process complexity.

Film formation. Film formation employs thermal oxidation to produce silicon dioxide (SiO_2) films, chemical vapor deposition to produce silicon, silicon dioxide, or silicon nitride (Si_3N_4) films, or vacuum evaporation/sputtering to produce metal films.

The atoms on the surface of a silicon single crystal from which integrated circuits are manufactured are chemically bound only in the direction of the bulk of the crystal, and not in the other or free direction. The resultant so-called silicon dangling bonds are very reactive and may bond to oxygen or nitrogen or other impurities from the atmosphere, so that a large variety of reactions can occur. Each of these reactions will result in different electrical properties for the silicon surface, a serious problem in designing a manufacturing process in which extremely large numbers of identically operating and reliable devices are produced on silicon chips. The solution to this dilemma is to tie up the dangling bonds with a chemically stable and electrically insulating film that will not interfere with the electrical characteristics of the silicon surface. A material with these properties that can be easily prepared in thin-film form on silicon is silicon dioxide.

The silicon dioxide film is made by the reaction of

Fig. 12. Vertical laminar-flow clean room for integrated-circuit fabrication.

a carefully cleaned and polished single-crystal silicon surface with an oxidant gas, usually oxygen or steam, at temperatures ranging from 1500 to 2200°F (800 to 1200°C) in a quartz-walled furnace tube (**Fig. 14*a***). The reaction occurs rapidly and exothermically on the silicon surface. As the oxide film grows, the rate of oxidation decreases, because the oxidant must transport to the silicon surface through the growing film. For large film thicknesses and at high oxidation temperatures, this transport controls the film growth kinetics, while for thin films the surface reaction is dominant. *See* Chemical bonding.

Chemical vapor deposition (CVD) is a gas-phase process where a film deposit is obtained by combining the appropriate gases in a reactant chamber at elevated temperatures. A typical CVD reaction (silox process) is given below. Figure 14*b* shows a cold-

$$SiH_4 + O_2 \xrightarrow[(750\text{–}930^\circ F)]{(400\text{–}500^\circ C)} \underset{\text{(deposits as film)}}{SiO_2\downarrow} + 2H_2\uparrow$$

walled, atmospheric-pressure CVD system where the silicon slice is heated by rf energy. Figure 14*c* shows a low-pressure CVD system where the slices and process gases are heated in a partially evacuated furnace tube. This low-pressure process produces very uniform film thicknesses. *See* Vapor deposition.

Evaporation or sputtering of metal coatings is performed in a vacuum, with metal transport being produced either by heat (evaporation) or bombarding ions (sputtering). The vacuum evaporator in Fig. 14*d* uses fixturing with planetary motion during evaporation. This achieves uniform metal thickness over surface topology on the silicon slice. *See* Crystal growth; Sputtering.

Impurity doping. The unique electronic properties of semiconductors are produced by substituting selected impurities at silicon lattice positions in the silicon crystal, a process called doping. The distortions in the chemical bonding due to the presence of impurities at lattice positions cause some of the bonding electrons in the crystal to have a higher energy than in a perfect crystal lattice and therefore be available for electronic conduction. Similarly, holes, which are the absence of bonding electrons, are produced by other kinds of impurities. Both electrons and holes can carry electric current. In order to construct complex integrated circuits, the impurities must be placed in adjacent regions in the semiconductor surface. The two predominant methods of doping semiconductor surfaces are thermal diffusion in high-temperature furnaces (Fig. 14*a*) and ion implantation.

In the diffusional doping process, the regions of the silicon surface to be doped are exposed to a concentration of the dopant while maintaining a high temperature. Boron and phosphorus are dopants which can be introduced by thermal diffusion at temperatures from 1500 to 2200°F (800 to 1200°C). At these temperatures the silicon lattice contains a significant number of vacant lattice sites, that is, crystal lattice sites with missing silicon atoms. The impurity atoms can migrate from vacant site to vacant site. The driving force for this diffusion process is the concentration gradient of impurity atoms. Near the silicon surface there exists a large concentration of dopant, while in the silicon only a small number of impurities exist. There is a tendency for these concentrations to be equalized, thereby eliminating the gradient. When

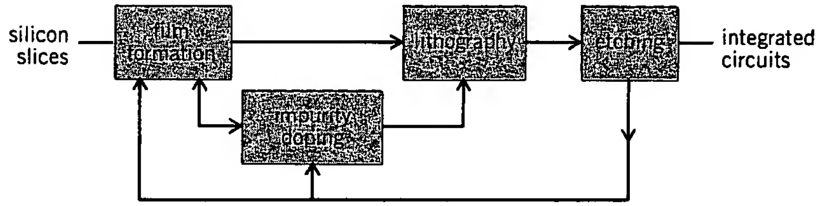


Fig. 13. Integrated-circuit fabrication sequence form. Fabrication normally proceeds in the direction of the arrows.

the impurity has diffused to the proper depth and is in the appropriate concentration in the silicon, the process is stopped. Other regions that are not to receive dopant are masked by using impenetrable films known as diffusion masks. *See* Crystal defects.

As device requirements become more stringent, very sharp diffusion profiles are needed so that the device size can be reduced. The solid-state diffusion process does not afford sufficient control for the most advanced device processes. For this purpose, the use of the direct implantation of impurity ions (electrically charged atoms) into the silicon lattice has been developed.

Ion implantation is also used when greater precision of dopant concentration is required or when a reduced temperature cycle is advantageous. Ion implantation makes use of intense, uniform beams of high-energy ions (typically 10–500 keV) of the desired dopant. These beams are formed in specialized accelerators such as Van de Graaff generators under high vacuum conditions (Fig. 14*e*). The beams can be focused, accelerated, and purified by using mass spectrometry techniques such as electrostatic plates and magnetic fields. The desired beam is then made to impinge on the silicon substrate which has appropriate masking so that the dopant beam impinges on the proper area of the silicon surface. The energy is sufficient for the ions in the beam to penetrate the silicon surface, leaving a distribution of dopant. The position of the peak of the distribution can be altered by altering the beam energy. The amount of dopant can be altered by the beam current and time of exposure. Damage is caused by the collisions of the ions in the beam with the atoms in the silicon lattice, but much of the damage can be removed by thermal annealing at temperatures of about 1500°F (800°C). Remarkably sharp dopant profiles of precise concentration can be achieved by using this technique. *See* Ion implantation.

Lithography. Lithography is necessary to define the small geometries required in integrated circuits. In lithography the silicon slice is coated uniformly with a thin film of photosensitive material called resist. If the lithography is to be performed optically, the integrated-circuit pattern to be transferred to the resist is first created on a glass plate or "mask." This pattern can then be transferred to the resist by a number of optical techniques. These techniques range from direct contact printing using a collimated source of ultra-violet light (Fig. 14*f*), to optical projection of a single integrated-circuit pattern with associated reduction (for example, 10:1, 1:1) and a precise *x-y* motion of the silicon slice (direct step-on-wafer; Fig. 14*g*). Electron-beam direct patterning can be performed, without a mask, by using a controllable electron beam and an electron-sensitive resist. Lithography has also been achieved with x-rays, by their projection through a special mask in close proximity to the slice. Direct step-on-wafer photolithography, the most advanced of

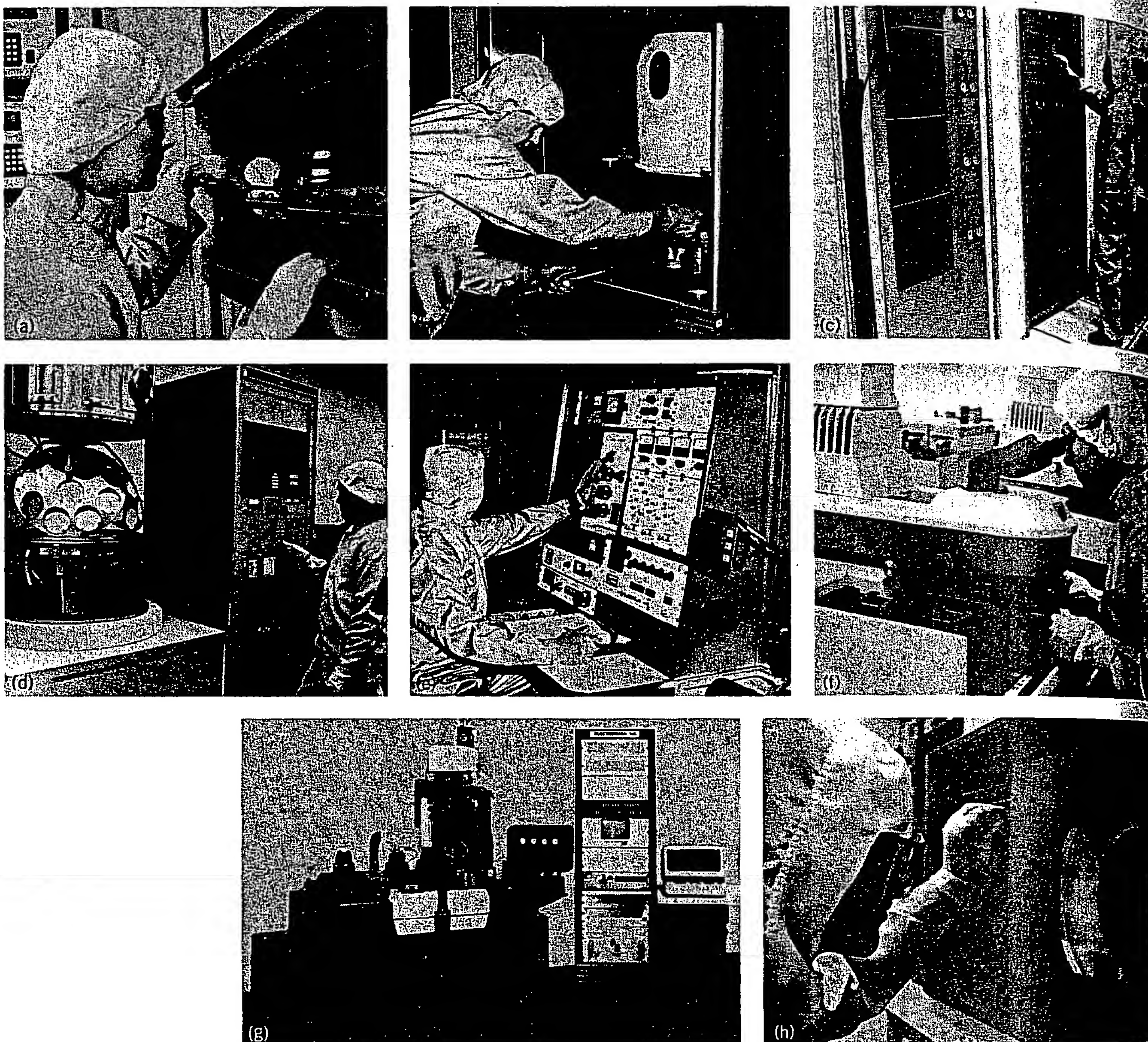


Fig. 14. Modern integrated-circuit fabrication equipment. (*a*) Diffusion furnace. (*b*) Atmospheric-pressure chemical vapor deposition (CVD). (*c*) Low-pressure CVD. (*d*) Vacuum evaporator. (*e*) Ion implanter. (*f*) Contact mask aligner. (*g*) Direct step-on-water machine. (*h*) Plasma etcher.

the optical lithographic techniques, is capable of defining 1 μm (4×10^{-5} in.) geometries. Electron-beam and x-ray lithography have demonstrated the capability to define features substantially smaller than 1 μm.

Etching. Etching is necessary to transfer the resist pattern achieved through lithography to the underlying surface. Traditionally, integrated-circuit fabrication has employed wet chemical processes to etch lines and features. These techniques utilize the chemical reactivity with an etchant of the material to be etched. The difference between the etch rate of the masking material and that of the substrate is related to this chemistry. The chemical etching of crystalline materials can be either isotropic or anisotropic. In isotropic etching the etchant attacks the crystal equally in all directions without regard to the different densities of atoms and structural features in the different directions in a crystal. Amorphous materials etch isotropically. Anisotropic etching takes advantage of different reactivities of the different crystal planes due to bonding and density differences. Usually anisotropic etches are milder etches that take full advantage of chemical differences. Anisotropic etching enables the construction of intricate patterns in silicon surfaces and therefore permits the practice of constructing devices in etched regions or on unetched mesa areas.

As with diffusion, wet chemical etching is limited in terms of size of the lines or features to be formed (no less than 3–4 μm or $1.2–1.6 \times 10^{-4}$ in.) and, more important, the aspect ratio of the features, that is, their height-to-width ratios. Dense packing and small device size require high-aspect-ratio etching. Dry plasma etching, reactive ion etching, and ion milling are advanced techniques being developed to overcome the limits of chemical etching. In plasma etching (Fig. 14*h*), the most advanced of these tech-